

# APPLICATION UNDER UNITED STATES PATENT LAWS

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Invention: SUBSTRATE TREATMENT DEVICE, SUBSTRATE TREATMENT METHOD, AND CLEANING METHOD FOR SUBSTRATE TREATMENT DEVICE

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## SPECIFICATION

SUBSTRATE TREATMENT DEVICE, SUBSTRATE TREATMENT METHOD, AND  
CLEANING METHOD FOR SUBSTRATE TREATMENT DEVICE

CROSS-REFERENCE TO THE INVENTION

5 [0001] This application is based upon and claims the benefit of priority from the prior Japanese Patent Application No. 2002-252273, filed on August 30, 2002; the entire contents of which are incorporated herein by reference.

10 10 BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

[0002] The present invention relates to a substrate treatment device that treats a substrate, a substrate treatment method, and a cleaning method for the substrate treatment device.

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2. DESCRIPTION OF THE RELATED ART

[0003] In recent years, there have been demands for higher speed and increasing density in manufacturing semiconductor devices. Accordingly, the hole diameter is becoming remarkably smaller, 20 resulting in a higher aspect ratio.

[0004] However, the increase in the aspect ratio tends to lower step coverage of a thin film such as a TiN film and a TiSiN film formed in holes. Such being the case, with the aim of forming thin films excellent in step coverage, a deposition device that forms 25 films while supplying treatment gases alternately has been presently drawing attention.

[0005] In forming the TiN film through the use of  $TiCl_4$  and  $NH_3$ , by such a deposition device, however, even when a trap is installed,

a large amount of yellow powder adheres to an inner wall of an exhaust pipe that is on a downstream side of the trap, concretely, the inner wall of the exhaust pipe whose inner pressure is maintained at an atmospheric pressure. Incidentally, this trap is intended for 5 capturing  $\text{NH}_4\text{Cl}$  that is a byproduct of the reaction. When a  $\text{TiSiN}$  film is formed through the use of  $\text{TiCl}_4$ ,  $\text{NH}_3$ , and  $\text{SiH}_2\text{Cl}_2$ , white powder in addition to the yellow powder adheres to the inner wall of the exhaust pipe. These powders deposit at every repetition of the film formation, which will be a cause of clogging the pipe. Therefore, 10 there is such a problem that frequent maintenance is necessary for removing the powders adhering to the inner wall of the exhaust pipe by opening the exhaust pipe. Incidentally, this problem may possibly occur also in a deposition device that forms films while supplying treatment gases simultaneously.

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#### BRIEF SUMMARY OF THE INVENTION

[0006] It is an object of the present invention to provide a substrate treatment device, a substrate treatment method, and a cleaning method for the substrate treatment device that are capable 20 of reducing the clogging of an exhaust system.

[0007] A substrate treatment device according to an aspect of the present invention is characterized in that it includes: a treatment chamber in which a substrate is to be placed; a supply system configured to supply at least two kinds of treatment gases to the 25 treatment chamber; an exhaust system having a pump, configured to exhaust the treatment gases from the treatment chamber; and a capturing unit interposed between the treatment chamber and the pump and containing fine grains, configured to capture by the fine grains

at least one kind of the treatment gas exhausted from the treatment chamber. According to this substrate treatment device of the present invention, a large amount of the treatment gas can be captured in the capturing unit. As a result, the clogging of the 5 exhaust system can be reduced.

[0008] The fine grains contained in the capturing unit are preferably zeolite. Zeolite may be either synthetic zeolite or natural zeolite. The use of zeolite makes it possible to inhibit the reaction of the treatment gas captured by zeolite with the other 10 treatment gas.

[0009] The capturing unit preferably captures the treatment gas that is liquid or solid at room temperature and at atmospheric pressure. Capturing such a treatment gas makes it possible to inhibit liquid or solid generated in the exhaust system.

[0010] The treatment gas captured by the capturing unit is preferably at least one of  $TiF_4$ ,  $TiCl_4$ ,  $TiBr_4$ ,  $TiI_4$ ,  $Ti[N(C_2H_5CH_3)_2]_4$  (TEMAT),  $Ti[N(CH_3)_2]_4$  (TDMAT),  $Ti[N(C_2H_5)_2]_4$  (TDEAT),  $TaF_5$ ,  $TaCl_5$ ,  $TaBr_5$ ,  $TaI_5$ ,  $Ta(NC(CH_3)_3)(N(C_2H_5)_2)_3$  (TBTDET),  $Ta(OC_2H_5)_5$ ,  $Al(CH_3)_3$ ,  $Zr(O-t(C_4H_9))_4$ ,  $ZrCl_4$ ,  $SiH_4$ ,  $Si_2H_6$ ,  $SiH_2Cl_2$ , and  $SiCl_4$ . Capturing these 20 treatment gases makes it possible to inhibit the generation of the powder in the exhaust system.

[0011] Another substrate treatment device according to the present invention is characterized in that it includes: a treatment chamber in which a substrate is to be placed; a supply system configured to supply at least two kinds of treatment gases to the treatment chamber; an exhaust system having a pump, configured to exhaust the treatment gases from the treatment chamber; and a capturing unit interposed between the treatment chamber and the pump,

configured to capture by a chemical action at least one kind of the treatment gas exhausted from the treatment chamber. The "chemical action" is accompanied by chemical reaction. The "chemical action" includes chemisorption. According to this substrate treatment 5 device of the present invention, a large amount of the treatment gas can be captured in the capturing unit. As a result, the clogging of the exhaust system can be reduced.

[0012] The capturing unit preferably has a metal oxide to capture the treatment gas. The use of the metal oxide enables reliable 10 capturing of the treatment gas. The metal oxide is preferably  $\text{Al}_2\text{O}_3$ . The use of  $\text{Al}_2\text{O}_3$  makes it possible to capture a large amount of the treatment gas even at reduced pressure.

[0013] Still another substrate treatment device of the present invention is characterized in that it includes: a treatment chamber 15 in which a substrate is to be placed; a supply system configured to supply at least two kinds of treatment gases to the treatment chamber; an exhaust system having at least one pump, configured to exhaust the treatment gases from the treatment chamber; and an inert gas supply system configured to supply an inert gas into the exhaust 20 system that is on a downstream side of the pump on a final stage. The inert gas is a gas inactive to the treatment gases. According to this substrate treatment device of the present invention, the liquefaction of the treatment gases can be inhibited. As a result, the clogging of the exhaust system can be reduced.

25 [0014] The inert gas preferably includes at least one of Ar, He, and  $\text{N}_2$ . The use of these gases enables reliable inhibition of the liquefaction of the treatment gas.

[0015] Yet another substrate treatment device of the present

invention is characterized in that it includes: a treatment chamber in which a substrate is to be placed; a supply system configured to supply at least two kinds of treatment gases into the treatment chamber; an exhaust system having at least one pump, configured to 5 exhaust the treatment gases from the treatment chamber; a heater configured to heat the exhaust system that is on a downstream side of the pump on a final stage. According to this substrate treatment device of the present invention, the liquefaction of the treatment gases can be inhibited. As a result, the clogging of the exhaust 10 system can be reduced.

[0016] The treatment gases may include at least one of  $TiF_4$ ,  $TiCl_4$ ,  $TiBr_4$ ,  $TiI_4$ ,  $Ti[N(C_2H_5CH_3)_2]_4$ ,  $Ti[N(CH_3)_2]_4$ ,  $Ti[N(C_2H_5)_2]_4$ ,  $TaF_5$ ,  $TaCl_5$ ,  $TaBr_5$ ,  $TaI_5$ ,  $Ta(NC(CH_3)_3)(N(C_2H_5)_2)_3$ ,  $Ta(OC_2H_5)_5$ ,  $Al(CH_3)_3$ ,  $Zr(O-t(C_4H_9))_4$ ,  $ZrCl_4$ ,  $SiH_4$ ,  $Si_2H_6$ ,  $SiH_2Cl_2$ , and  $SiCl_4$ . These gases are gases 15 that may possibly cause the clogging of the exhaust system, but according to this substrate treatment device of the present invention, the clogging of the exhaust system can be reduced, which allows the use of these gases.

[0017] The substrate treatment device preferably further 20 includes a supply controller configured to control the supply system to supply the treatment gases alternately. When the supply controller is provided, a high-quality film can be formed.

[0018] A substrate treatment method according to another aspect of the present invention includes: a metal-containing gas supply 25 step of supplying a metal-containing gas at a first flow rate into a treatment chamber while the treatment chamber has a substrate placed therein; a metal-containing gas exhaust step of exhausting the metal-containing gas from the treatment chamber via an exhaust

system; a nitriding agent gas supply step of supplying a nitriding agent gas into the treatment chamber at a second flow rate that is 10 times as large as the first flow rate or at a larger rate; and a nitriding agent exhaust step of exhausting the nitriding agent 5 gas from the treatment chamber via the exhaust system. The metal-containing gas exhaust step may be conducted either after the metal-containing gas supply step or during the metal-containing gas supply step. The nitriding agent gas supply step may be conducted either after the metal-containing gas supply step or during the metal-containing gas supply step. The nitriding agent gas exhaust 10 step may be conducted either after the nitriding agent gas supply step or during the nitriding agent gas supply step. According to this substrate treatment method of the present invention, the clogging of the exhaust system can be reduced.

15 [0019] The nitriding agent gas is preferably supplied at a flow rate of 300 sccm to 1000 sccm. The supply of the nitriding agent gas at such a flow rate makes it possible to reduce the clogging of the exhaust system reliably.

[0020] The metal-containing gas may include at least one of  $TiF_4$ , 20  $TiCl_4$ ,  $TiBr_4$ ,  $TiI_4$ ,  $Ti[N(C_2H_5CH_3)_2]_4$ ,  $Ti[N(CH_3)_2]_4$ ,  $Ti[N(C_2H_5)_2]_4$ ,  $TaF_5$ ,  $TaCl_5$ ,  $TaBr_5$ ,  $TaI_5$ , and  $Ta(NC(CH_3)_3)(N(C_2H_5)_2)_3$ . These gases are gases that may possibly cause the clogging of the exhaust system, but according to this substrate treatment method of the present invention, the clogging of the exhaust system can be reduced, which 25 allows the use of these gases.

[0021] The nitriding agent gas preferably includes  $NH_3$ . When it includes  $NH_3$ , the clogging of the exhaust system can be more reliably reduced.

[0022] A cleaning method for a substrate treatment device according to still another aspect of the present invention is characterized in that it includes: a substrate treatment device preparing step of preparing a substrate treatment device that treats 5 a substrate by supplying a metal-containing gas and a nitriding agent gas to the substrate; and a nitriding agent gas supply step of supplying a nitriding agent gas into an exhaust system of the substrate treatment device while the substrate treatment device does not have the substrate placed therein. According to this 10 cleaning method for the substrate treatment device of the present invention, the clogging of the exhaust system can be reduced.

[0023] The nitriding agent gas supplied in the nitriding agent gas supply step is preferably supplied at a flow rate larger than a flow rate of the nitriding agent gas supplied for the treatment. 15 The supply of the nitriding agent gas at such a flow rate makes it possible to reduce the clogging of the exhaust system reliably.

[0024] The nitriding agent gas supplied in the nitriding agent gas supply step is preferably supplied at a flow rate of 300 sccm to 1000 sccm. The supply of the nitriding agent gas at such a flow 20 rate makes it possible to more reliably reduce the clogging of the exhaust system.

[0025] The metal-containing gas may include at least one of  $TiF_4$ ,  $TiCl_4$ ,  $TiBr_4$ ,  $TiI_4$ ,  $Ti[N(C_2H_5CH_3)_2]_4$ ,  $Ti[N(CH_3)_2]_4$ ,  $Ti[N(C_2H_5)_2]_4$ ,  $TaF_5$ ,  $TaCl_5$ ,  $TaBr_5$ ,  $TaI_5$ , and  $Ta(NC(CH_3)_3)(N(C_2H_5)_2)_3$ . These gases are gases 25 that may possibly cause the clogging of the exhaust system, but according to this cleaning method for the substrate treatment device of the present invention, the clogging of the exhaust system can be reduced, which allows the use of these gases.

[0026] The nitriding agent gas preferably includes NH<sub>3</sub>. When it includes NH<sub>3</sub>, the clogging of the exhaust system can be more reliably reduced.

[0027] Another cleaning method of a substrate treatment device of the present invention is characterized in that it includes a nitriding agent gas supply step of supplying a nitriding agent gas into an exhaust system of the substrate treatment device that treats a substrate by supplying a metal-containing gas and a nitriding agent gas, while the substrate treatment device does not have the substrate placed therein. According to this cleaning method of the present invention, the clogging of the exhaust system can be reduced.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0028] FIG. 1 is a schematic block diagram showing a deposition device according to a first embodiment.

[0029] FIG. 2 is a schematic vertical sectional view of a capturing unit according to the first embodiment.

[0030] FIG. 3 is a flowchart showing the flow of the treatment conducted in the deposition device according to the first embodiment.

[0031] FIG. 4A to FIG. 4D are views schematically showing the treatment conducted in the deposition device according to the first embodiment.

[0032] FIG. 5 is a schematic block diagram of a deposition device according to a second embodiment.

[0033] FIG. 6 is a schematic vertical sectional view of a capturing unit according to the second embodiment.

[0034] FIG. 7 is a flow chart showing the flow of the treatment

conducted in the deposition device according to the second embodiment.

[0035] FIG. 8A and FIG. 8B are views schematically showing the treatment conducted in the deposition device according to the second 5 embodiment.

[0036] FIG. 9 is a schematic block diagram of a deposition device according to a third embodiment.

[0037] FIG. 10 is a flowchart showing the flow of the treatment conducted in the deposition device according to the third 10 embodiment.

[0038] FIG. 11 is a view schematically showing the treatment conducted in the deposition device according to the third embodiment.

[0039] FIG. 12 is a schematic block diagram of a deposition device 15 according to a fourth embodiment.

[0040] FIG. 13 is a flowchart showing the flow of the treatment conducted in the deposition device according to the fourth embodiment.

[0041] FIG. 14 is a view schematically showing the treatment 20 conducted in the deposition device according to the fourth embodiment.

[0042] FIG. 15 is a flowchart showing the flow of the treatment conducted in a deposition device according to a fifth embodiment.

[0043] FIG. 16 is a flowchart showing the flow of the overall 25 treatment conducted in a deposition device according to a sixth embodiment.

[0044] FIG. 17 is a flowchart showing the flow of the treatment for one piece of wafer conducted in the deposition device according

to the sixth embodiment.

[0045] FIG. 18 is a view schematically showing the treatment conducted in the deposition device according to the sixth embodiment.

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#### DETAILED DESCRIPTION OF THE INVENTION

##### (First Embodiment)

[0046] Hereinafter, a deposition device according to a first embodiment of the present invention will be explained. FIG. 1 is 10 a schematic block diagram of the deposition device according to this embodiment.

[0047] As shown in FIG. 1, a deposition device 1 has a chamber 2 formed of, for example, aluminum or stainless steel. Incidentally, surface treatment, for example, the treatment of anodized aluminum 15 may be applied to the surface of the chamber 2. The chamber 2 has an opening 2A formed in a side portion thereof, and near the opening 2A, a gate valve 3 intended for allowing a semiconductor wafer (hereinafter, simply referred to as a 'wafer') W to be carried into or carried out of the chamber 2 is attached.

20 [0048] A susceptor 4 in a substantially disc shape to place the wafer W thereon is disposed in the chamber 2. The susceptor 4 is formed of, for example, ceramics such as AlN or Al<sub>2</sub>O<sub>3</sub>. A heater 5 for heating the susceptor 4 to a predetermined temperature is provided in the susceptor 4. When the heater 5 heats the susceptor 25 4 to the predetermined temperature, the wafer W placed on the susceptor 4 is heated to the predetermined temperature.

[0049] Holes 4A intended for a wafer up/down are formed in a vertical direction at three places of the susceptor 4. Wafer

up/down pins 6 insertable into the holes 4A are provided at lower portions of the holes 4A respectively. The wafer up/down pins 6 are fixed onto a wafer up/down pin support table 7 so as to vertically stand. An air cylinder 8 is fixed to the wafer up/down pin support table 7. When a rod 8A of the air cylinder 8 is contracted by the drive of the air cylinder 8, the wafer up/down pins 6 are moved down so that the wafer W is placed on the susceptor 4. When the rod 8A is extended by the drive of the air cylinder 8, the wafer up/down pins 6 are moved up so that the wafer W is detached from the susceptor 10 4. A contractible/extendable bellows 9 covering the rod 8A is disposed in the chamber 2. By covering the rod 8A with the bellows 9, airtightness inside the chamber 2 is maintained.

[0050] An opening is formed in an upper portion of the chamber 2. A showerhead 10 to introduce  $TiCl_4$  and  $NH_3$  to the susceptor 4 15 is inserted in the opening. The showerhead 10 is divided into a  $TiCl_4$  introducing portion 10A and an  $NH_3$  introducing portion 10B. A large number of  $TiCl_4$  introducing ports through which  $TiCl_4$  is supplied are formed in the  $TiCl_4$  introducing portion 10A. Similarly, a large number of  $NH_3$  introducing ports through which  $NH_3$  is supplied 20 are formed in the  $NH_3$  introducing portion 10B.

[0051] A  $TiCl_4$  supply system 20 to supply  $TiCl_4$  to the  $TiCl_4$  introducing portion 10A is connected to the  $TiCl_4$  introducing portion 10A of the showerhead 10. An  $NH_3$  supply system 30 to supply  $NH_3$  to the  $NH_3$  introducing portion 10B is connected to the  $NH_3$  introducing 25 portion 10B.

[0052] The  $TiCl_4$  supply system 20 has a  $TiCl_4$  supply source 21 storing  $TiCl_4$  therein. A  $TiCl_4$  supply pipe 22 having one end connected to the  $TiCl_4$  introducing portion 10A is connected to the

TiCl<sub>4</sub> supply source 21. A valve 23 and a mass flow controller (MFC) 24 to control the flow rate of TiCl<sub>4</sub> are disposed in the TiCl<sub>4</sub> supply pipe 22. When the valve 23 is opened while the mass flow controller 24 is in a controlled state, TiCl<sub>4</sub> is supplied to the TiCl<sub>4</sub> introducing portion 10A from the TiCl<sub>4</sub> supply source 21 at a predetermined flow rate.

5 [0053] The NH<sub>3</sub> supply system 30 has an NH<sub>3</sub> supply source 31 storing NH<sub>3</sub> therein. An NH<sub>3</sub> supply pipe 32 having one end connected to the NH<sub>3</sub> introducing portion 10B is connected to the NH<sub>3</sub> supply source 10 31. A valve 33 and a mass flow controller 34 to control the flow rate of NH<sub>3</sub> are disposed in the NH<sub>3</sub> supply pipe 32. When the valve 33 is opened while the mass flow controller 34 is in a controlled state, NH<sub>3</sub> is supplied to the showerhead 10 from the NH<sub>3</sub> supply source 31 at a predetermined flow rate.

15 [0054] A valve controller 35 that controls the valves 23, 33 so as to alternately open the valve 23, 33 is electrically connected to the valves 23, 33. Owing to such control over the valves 23, 33 by the valve controller 35, a TiN film excellent in step coverage is formed on the wafer W.

20 [0055] An exhaust system 40 to exhaust gases such as TiCl<sub>4</sub> and NH<sub>3</sub> is connected to a bottom portion of the chamber 2. The exhaust system 40 has an auto-pressure controller (APC) 41 to control the pressure inside the chamber 2. When conductance is adjusted by the auto-pressure controller 41, the pressure inside the chamber 2 is 25 controlled at a predetermined pressure.

[0056] An exhaust pipe 42 is connected to the auto-pressure controller 41. The other end of the exhaust pipe 42 is open to the atmosphere. In the exhaust pipe 42, a main valve 43, a turbo

molecular pump 44, a trap 45, a capturing unit 46, a valve 47, a dry pump 48, and a capturing unit 49 are arranged in this order from an upstream side to a downstream side.

[0057] The turbo molecular pump 44 conducts high evacuation. The 5 high evacuation by the turbo molecular pump 44 causes the pressure inside the chamber 2 to be maintained at a predetermined pressure. The turbo molecular pump 44 is also intended for exhausting excessive  $TiCl_4$ ,  $NH_3$ ,  $TiN$ ,  $NH_4Cl$ , and so on from the chamber 2.

[0058] The trap 45 is intended for capturing  $NH_4Cl$  contained in 10 an exhaust gas to remove  $NH_4Cl$  from the exhaust gas. The trap 45 has a housing 45A in which a flow-in port for letting the exhaust gas in therethrough and a flow-out port for letting the exhaust gas out therethrough are formed. A plate member 45B is disposed in the housing 45A, and the plate member 45B is cooled by a not-shown cooler. 15 When powder of  $NH_4Cl$  comes into contact with the cooled plate member 45B, the plate member 45B adsorbs the powder of  $NH_4Cl$  by physical adsorption, so that  $NH_4Cl$  is removed from the exhaust gas.

[0059] The dry pump 48 is intended for assisting the turbo molecular pump 44. The dry pump 48 also conducts low evacuation 20 of the inside of the chamber 2. When the pressure of a subsequent stage of the turbo molecular pump 44 is reduced by the dry pump 48, the exhaust rate of the turbo molecular pump 44 can be increased.

[0060] A roughing out pipe 50 for use in low evacuation by the dry pump 48 is connected to the exhaust pipe 42 between the valve 25 47 and the dry pump 48. The other end of the roughing out pipe 50 is connected to the exhaust pipe 42 between the auto-pressure controller 41 and the main valve 43. A valve 51 is disposed in the roughing out pipe 50.

[0061] The capturing units 46, 49 are intended for capturing  $TiCl_4$  contained in the exhaust gas to remove  $TiCl_4$  from the exhaust gas. The capturing unit 46 will be explained in detail below. FIG. 2 is a schematic vertical sectional view of the capturing unit 46 according to this embodiment.

[0062] As shown in FIG. 2, the capturing unit 46 has a housing 46C in which a flow-in port 46A for letting the exhaust gas in therethrough and a flow-out port 46B for letting the exhaust gas out therethrough are formed. Fine-grained synthetic zeolite 46D is contained in the housing 46C. When  $TiCl_4$  contained in the exhaust gas comes into contact with the synthetic zeolite 46D, the synthetic zeolite 46D adsorbs  $TiCl_4$  by physical adsorption, so that  $TiCl_4$  is removed from the exhaust gas.

[0063] Hereinafter, the flow of the treatment conducted in the deposition device 1 will be explained, following FIG. 3 to FIG. 4D. FIG. 3 is a flowchart showing the flow of the treatment conducted in the deposition device 1 according to this embodiment, and FIG. 4A to FIG. 4D are views schematically showing the treatment conducted in the deposition device 1 according to this embodiment.

[0064] First, the main valve 43 and the valve 47 are closed, and while the valve 51 is in an open state, the dry pump 48 operates to conduct low evacuation of the inside of the chamber 2. Thereafter, when the pressure in the chamber 2 is reduced to some extent, the valve 51 is closed and at the same time, the main valve 43 and the valve 47 are opened, so that the low evacuation by the dry pump 48 is changed to the high evacuation by the turbo molecular pump 44 (Step 1A). Note that the dry pump 48 is kept operating even after this change.

[0065] After the pressure inside the chamber 2 is reduced to, for example,  $1.33 \times 10^{-2}$  Pa or lower, the gate valve 3 is opened and a not-shown transfer arm holding the wafer W extends to carry the wafer W into the chamber 2 (Step 2A).

5 [0066] Thereafter, the transfer arm contracts and the wafer W is placed on the wafer up/down pins 6. After the wafer W is placed on the wafer up/down pins 6, the wafer up/down pins 6 are moved down by the drive of the air cylinder 8, so that the wafer W is placed on the susceptor 4 having been heated to about 300°C to about 450°C  
10 (Step 3A).

[0067] After the temperature of the wafer W is raised, the valve 23 is opened while the pressure inside the chamber 2 is kept at about 50 Pa to about 400 Pa, so that  $TiCl_4$  is introduced to the wafer W from the  $TiCl_4$  introducing portion 10A at a flow rate of about 30  
15 sccm, as shown in FIG. 4A (Step 4A). When the introduced  $TiCl_4$  comes into contact with the wafer W,  $TiCl_4$  is adsorbed over the surface of the wafer W.

[0068] After a predetermined period of time passes, the valve 23 is closed to stop the supply of  $TiCl_4$ , and at the same time,  $TiCl_4$   
20 remaining in the chamber 2 is exhausted from the chamber 2, as shown in FIG. 4B (Step 5A). Note that the pressure inside the chamber 2 at the time of the exhausting becomes  $6.67 \times 10^{-2}$  Pa or lower.

[0069] After a predetermined period of time passes, the valve 33 is opened, so that  $NH_3$  is introduced to the wafer W from the  $NH_3$  j  
25 introducing portion 10B at a flow rate of about 100 sccm, as shown in FIG. 4C (Step 6A). When the introduced  $NH_3$  comes into contact with  $TiCl_4$  adsorbed by the wafer W,  $TiCl_4$  and  $NH_3$  react with each other, so that a TiN film is formed on the wafer W.

[0070] After a predetermined period of time passes, the valve 33 is closed to stop the supply of  $\text{NH}_3$ , and at the same time,  $\text{NH}_3$  and so on remaining in the chamber 2 are exhausted from the chamber 2, as shown in FIG. 4D (Step 7A). Note that the pressure inside the 5 chamber 2 at the time of the exhausting becomes  $6.67 \times 10^{-2}$  Pa or lower.

[0071] After a predetermined period of time passes, it is judged by a not-shown central controller whether or not 200 cycles of the treatment have been conducted, with the processes from Step 4A to 10 Step 7A being one cycle (Step 8A). When it is judged that 200 cycles of the treatment have not been conducted, the processes from Step 4A to Step 7A are conducted again.

[0072] When it is judged that 200 cycles of the treatment have been conducted, the wafer up/down pins 6 are moved up by the drive 15 of the air cylinder 8, so that the wafer W is detached from the susceptor 4 (Step 9A). Note that when 200 cycles of the treatment are conducted, the TiN film with a thickness of about 10 nm is formed on the wafer W.

[0073] Thereafter, after the gate valve 3 is opened, the not-20 shown transfer arm extends to hold the wafer W. Finally, the transfer arm contracts to carry the wafer W out of the chamber 2 (Step 10A).

[0074] In this embodiment, since the capturing unit 46 containing the fine grains is disposed between the chamber 2 and the dry pump 25 48, the clogging of the exhaust pipe 42 can be reduced. To be more specific, yellow powder adhering to an inner wall of the exhaust pipe is generated by the reaction between  $\text{TiCl}_4$  and  $\text{NH}_3$  that are exhausted from the chamber. Concretely, the yellow powder is  $\text{TiCl}_4 \cdot$

n NH<sub>3</sub> (n = 2, 4), which is generated by the reaction between TiCl<sub>4</sub> and NH<sub>3</sub> at about 150°C or lower. The possible reason why a large amount of the yellow powder adheres to the inner wall of the exhaust pipe maintained at the atmospheric pressure is that TiCl<sub>4</sub> is

5 liquefied or a large amount of TiCl<sub>4</sub> adheres to the inner wall of the exhaust pipe. Concretely, as for the liquefaction of TiCl<sub>4</sub>, when TiCl<sub>4</sub> is liquefied, it is difficult for the liquefied TiCl<sub>4</sub> to move. When NH<sub>3</sub> flows therein, the reaction between TiCl<sub>4</sub> and NH<sub>3</sub> occurs one after another. This is the possible reason for the adhesion

10 of a large amount of the yellow powder to the inner wall of the exhaust pipe maintained at the atmospheric pressure. As for the adhesion of a large amount of TiCl<sub>4</sub> to the inner wall of the exhaust pipe, at the atmospheric pressure, TiCl<sub>4</sub> is more easily adsorbed by the inner wall of the exhaust pipe and the adsorbed TiCl<sub>4</sub> is more

15 difficult to be detached than at the reduced pressure. Therefore, an adhesion amount of TiCl<sub>4</sub> to the inner wall of the exhaust pipe increases. When NH<sub>3</sub> flows therein, the reaction between TiCl<sub>4</sub> and NH<sub>3</sub> occurs one after another. This is the possible reason for the adhesion of a large amount of the yellow powder to the inner wall

20 of the exhaust pipe 42 maintained at the atmospheric pressure. Therefore, when TiCl<sub>4</sub> is captured at the reduced pressure, the generation of the yellow powder is inhibited, so that the adhesion of the yellow powder to the inner wall of the exhaust pipe maintained at the atmospheric pressure is inhibited. Here, a trap provided

25 in a conventional deposition device is installed under the condition of the reduced pressure, and therefore, this trap is also likely to be capable of capturing TiCl<sub>4</sub>, but the surface area of the trap is small. Accordingly, an amount of TiCl<sub>4</sub> captured by the trap is

very small, which is the possible reason for not allowing effective inhibition of the generation of the yellow powder. In this embodiment, on the other hand, since  $TiCl_4$  is captured by the fine grains, the surface area is large, so that a large amount of  $TiCl_4$  can be captured. Consequently, it is possible to greatly reduce the yellow powder adhering to the inner wall of the exhaust pipe 42, resulting in the reduction in the clogging of the exhaust pipe 42. As a result, maintenance frequency can be lowered.

[0075] In this embodiment, owing to the use of the synthetic zeolite 46D,  $TiCl_4$  adsorbed by the synthetic zeolite 46D does not easily react with  $NH_3$  that flows in thereafter. As a result, reliable inhibition of the generation of the yellow powder is realized.

[0076] In this embodiment,  $TiCl_4$  and  $NH_3$  are alternately supplied, and even in such a case, the generation of the yellow powder can be reliably inhibited. Specifically, the comparison of the alternate supply of  $TiCl_4$  and  $NH_3$  with the simultaneous supply of  $TiCl_4$  and  $NH_3$  shows that an amount of  $TiCl_4$  exhausted from the chamber 2 is larger in the alternate supply. Therefore, an amount of the generated yellow powder becomes larger in the alternate supply than in the simultaneous supply. In this embodiment, since  $TiCl_4$  can be reliably captured, the generation of the yellow powder can be reliably inhibited even when  $TiCl_4$  and  $NH_3$  are alternately supplied.

(Second Embodiment)

[0077] Hereinafter, a second embodiment of the present invention will be explained. Note that some of the contents of this embodiment and embodiments thereafter that are the same as those in the previous embodiment will be omitted in the explanation. In this embodiment,

the explanation will be given on an example where a capturing unit contains aluminum oxide ( $Al_2O_3$ ) in addition to synthetic zeolite.

5 [0078] FIG. 5 is a schematic block diagram of a deposition device according to this embodiment. As shown in FIG. 5, a deposition device 1 has an  $SiH_2Cl_2$  supply system 60. The  $SiH_2Cl_2$  supply system 60 has an  $SiH_2Cl_2$  supply source 61 storing  $SiH_2Cl_2$  therein. An  $SiH_2Cl_2$  supply pipe 62 having one end connected to a  $TiCl_4$  supply pipe 22 is connected to the  $SiH_2Cl_2$  supply source 61. A valve 63 and a mass flow controller 64 to control the flow rate of  $SiH_2Cl_2$ , are disposed in the  $SiH_2Cl_2$  supply pipe 62. The valve 63 is opened while the valve 23 is in a closed state and the mass flow controller 64 is in a controlled state, so that  $SiH_2Cl_2$  is supplied to a  $TiCl_4$  introducing portion 10A from the  $SiH_2Cl_2$  supply source 61 at a predetermined flow rate.

10 [0079] A valve controller 35 to control the valves 23, 33, 63 so as to open the valve 23, 33, 63 by turns is electrically connected to the valve 63. Owing to such control over the valves 23, 33, 63 by the valve controller 35, a  $TiSiN$  film excellent in step coverage is formed on a wafer W.

15 [0080] Next, a capturing unit 46 in this embodiment will be explained. FIG. 6 is a schematic vertical sectional view of the capturing unit 46 according to this embodiment. As shown in FIG. 6, fine-grained synthetic zeolite 46D and fine-grained aluminum oxide 46E are put in an alternate layered state in the capturing unit 46. When  $SiH_2Cl_2$  contained in an exhaust gas comes into contact with the aluminum oxide 46E,  $SiH_2Cl_2$  is adsorbed by the aluminum oxide 46E by chemisorption, so that  $SiH_2Cl_2$  is removed from the exhaust gas.

[0081] Hereinafter, the flow of the treatment conducted in the deposition device 1 will be explained, following FIG. 7 to FIG. 8B. FIG. 7 is a flowchart showing the flow of the treatment conducted in the deposition device 1 according to this embodiment, and FIG. 5 8A and FIG. 8B are views schematically showing the treatment conducted in the deposition device 1 according to this embodiment.

[0082] A dry pump 48 is operated to conduct low evacuation of the inside of a chamber 2. Thereafter, the low evacuation by the dry pump 48 is changed to high evacuation by a turbo molecular pump 44 10 (Step 1B).

[0083] After the pressure inside the chamber 2 is reduced to, for example,  $1.33 \times 10^{-2}$  Pa or lower, a not-shown transfer arm holding the wafer W extends to carry the wafer W into the chamber 2 (Step 2B). Thereafter, wafer up/down pins 6 are moved down to place the 15 wafer W on a susceptor 4 (Step 3B).

[0084] After the temperature of the wafer W is raised, the valve 23 is opened while the pressure inside the chamber 2 is kept at about 50 Pa to about 400 Pa, so that  $TiCl_4$  is introduced from the  $TiCl_4$  introducing portion 10A (Step 4B). After a predetermined period 20 of time passes, the valve 23 is closed to stop the supply of  $TiCl_4$  and at the same time,  $TiCl_4$  remaining in the chamber 2 is exhausted from the chamber 2 (Step 5B).

[0085] After a predetermined period of time passes, the valve 63 is opened, so that  $SiH_2Cl_2$  is introduced from the  $TiCl_4$  introducing 25 portion 10A at a flow rate of about 30 sccm, as shown in FIG. 8A (Step 6B). When the introduced  $SiH_2Cl_2$  comes into contact with  $TiCl_4$  adsorbed by the wafer W,  $TiCl_4$  and  $SiH_2Cl_2$  react with each other, so that a film in which Ti and Si are bonded together is formed on

the wafer W. After a predetermined period of time passes, the valve 61 is closed to stop the supply of  $\text{SiH}_2\text{Cl}_2$ , and at the same time,  $\text{SiH}_2\text{Cl}_2$ , and so on remaining in the chamber 2 are exhausted from the chamber 2, as shown in FIG. 8B (Step 7B).

5 [0086] After a predetermined period of time passes, the valve 33 is opened, so that  $\text{NH}_3$  is introduced from an  $\text{NH}_3$  introducing portion 10B (Step 8B). When the introduced  $\text{NH}_3$  comes into contact with the film in which Ti and Si are bonded together on the wafer W, the film in which Ti and Si are bonded together react with  $\text{NH}_3$ , so that a 10 TiSiN film is formed on the wafer W. After a predetermined period of time passes, the valve 33 is closed to stop the supply of  $\text{NH}_3$ , and at the same time,  $\text{NH}_3$ , and so on remaining in the chamber 2 are exhausted from the chamber 2 (Step 9B).

15 [0087] After a predetermined period of time passes, it is judged whether or not 200 cycles of the treatment, with the processes from Step 4B to Step 9B being one cycle, have been conducted (Step 10B). When it is judged that 200 cycles of the treatment have not been conducted, the processes from Step 4B to Step 9B are conducted again.

20 [0088] When it is judged that 200 cycles of the treatment have been conducted, the wafer up/down pins 6 are moved up, so that the wafer W is detached from the susceptor 4 (Step 11B). Finally, the wafer W is carried out of the chamber 2 by the not-shown transfer arm (Step 12B).

25 [0089] In this embodiment, since the capturing unit 46 containing the aluminum oxide 46E is disposed between the chamber 2 and the dry pump 48, the clogging of an exhaust pipe 42 can be reduced. To be more specific, white powder adhering to an inner wall of the exhaust pipe is generated by the reaction between  $\text{SiH}_2\text{Cl}_2$ , and  $\text{NH}_3$

that are exhausted from the chamber. Specifically, the white powder is  $\text{NH}_4\text{Cl}$ . The possible reason why a large amount of the white powder adheres to the inner wall of the exhaust pipe maintained at the atmospheric pressure is that a large amount of  $\text{SiH}_2\text{Cl}_2$  adheres to

5 the inner wall of the exhaust pipe. Concretely, as described above, at the atmospheric pressure,  $\text{SiH}_2\text{Cl}_2$  is more easily adsorbed by the inner wall of the exhaust pipe and the adsorbed  $\text{SiH}_2\text{Cl}_2$  is more difficult to be detached than at the reduced pressure. Therefore, an adhesion amount of  $\text{SiH}_2\text{Cl}_2$  to the inner wall of the exhaust pipe

10 increases. When  $\text{NH}_3$  flows therein, the reaction between  $\text{SiH}_2\text{Cl}_2$  and  $\text{NH}_3$  occurs one after another. This is the possible reason for the adhesion of a large amount of the white powder to an inner wall of the exhaust pipe maintained at the atmospheric pressure. Here,  $\text{NH}_4\text{Cl}$  is also captured in a trap provided in a conventional deposition

15 device, but  $\text{NH}_4\text{Cl}$  that this trap is capable of capturing is mainly  $\text{NH}_4\text{Cl}$  generated in the chamber, and  $\text{NH}_4\text{Cl}$  generated at the atmospheric pressure cannot be captured. This is the possible reason for not allowing effective inhibition of the generation of the white powder. In this embodiment, on the other hand,  $\text{SiH}_2\text{Cl}_2$ ,

20 that is a generating source of  $\text{NH}_4\text{Cl}$  is captured in advance at the reduced pressure, so that it is possible to greatly reduce the white powder adhering to the inner wall of the exhaust pipe 42, thereby reducing the clogging of the exhaust pipe 42. As a result, maintenance frequency can be lowered.

25 [0090] In this embodiment, the aluminum oxide 46E captures  $\text{SiH}_2\text{Cl}_2$  by chemisorption. Here, since chemisorption is the adsorption by chemical reaction, even a gas can be adsorbed reliably. Accordingly, an amount of  $\text{SiH}_2\text{Cl}_2$  captured in this case is larger than that when

$\text{SiH}_2\text{Cl}_2$  is captured by physical adsorption.

[0091] In this embodiment, since the aluminum oxide 46E is contained in a fine-grained state, so that the surface area thereof is large. Therefore, a larger amount of  $\text{SiH}_2\text{Cl}_2$ , can be captured.

5 [0092] In this embodiment,  $\text{TiCl}_4$ ,  $\text{SiH}_2\text{Cl}_2$ , and  $\text{NH}_3$ , are supplied by turns, and even in such a case, the generation of the white powder can be reliably inhibited. Specifically, the comparison of the supply of  $\text{TiCl}_4$ ,  $\text{SiH}_2\text{Cl}_2$ , and  $\text{NH}_3$ , by turns with the simultaneous supply of  $\text{TiCl}_4$ ,  $\text{SiH}_2\text{Cl}_2$ , and  $\text{NH}_3$ , shows that an amount of  $\text{SiH}_2\text{Cl}_2$ , exhausted 10 from the chamber 2 is larger in the supply by turns. Therefore, an amount of the generated white powder is larger in the supply by turns than in the simultaneous supply. In this embodiment, since  $\text{SiH}_2\text{Cl}_2$  can be reliably captured, the generation of the white powder can be reliably inhibited even when  $\text{TiCl}_4$ ,  $\text{SiH}_2\text{Cl}_2$ , and  $\text{NH}_3$ , are 15 supplied by turns. Since the capturing unit 46E also contains the synthetic zeolite 46D, the same effect as in the first embodiment is obtainable.

(Third Embodiment)

[0093] Hereinafter, a third embodiment of the present invention 20 will be explained. In this embodiment, the explanation will be given on an example where provided is an  $\text{N}_2$  supply system to supply  $\text{N}_2$  into an exhaust pipe that is on a downstream side of a dry pump.

[0094] FIG. 9 is a schematic block diagram of a deposition device according to this embodiment. As shown in FIG. 9, an  $\text{N}_2$  supply system 25 70 to supply  $\text{N}_2$  into an exhaust pipe 42 is connected to the exhaust pipe 42 that is on a downstream side of a dry pump 48. The  $\text{N}_2$  supply system 70 has an  $\text{N}_2$  supply source 71 storing  $\text{N}_2$  therein. An  $\text{N}_2$  supply pipe 72 having one end connected to the exhaust pipe 42 that is on

the downstream side of the dry pump 48 is connected to the N<sub>2</sub> supply source 71. A valve 73 and a mass flow controller 74 to control the flow rate of N<sub>2</sub> are disposed in the N<sub>2</sub> supply pipe 72. When the valve 73 is opened while the mass flow controller 74 is in a controlled 5 state, N<sub>2</sub> is supplied into the exhaust pipe 42 from the N<sub>2</sub> supply source 71 at a predetermined flow rate.

[0095] Hereinafter, the flow of the treatment conducted in a deposition device 1 will be explained, following FIG. 10 and FIG. 11. FIG. 10 is a flowchart showing the flow of the treatment 10 conducted in the deposition device 1 according to this embodiment, and FIG. 11 is a view schematically showing the treatment conducted in the deposition device 1 according to this embodiment.

[0096] The dry pump 48 is operated to conduct low evacuation of the inside of a chamber 2. Thereafter, the low evacuation by the 15 dry pump 48 is changed to high evacuation by a turbo molecular pump 44 (Step 1C).

[0097] After the pressure inside the chamber 2 is reduced to, for example,  $1.33 \times 10^{-2}$  Pa or lower, a not-shown transfer arm holding a wafer W extends to carry the wafer W into the chamber 2 (Step 2C). 20 Thereafter, wafer up/down pins 6 are moved down to place the wafer W on a susceptor 4 (Step 3C).

[0098] After the temperature of the wafer W is raised, a valve 23 is opened while the pressure inside the chamber 2 is kept at about 25 50 Pa to about 400 Pa, so that TiCl<sub>4</sub> is introduced from a TiCl<sub>4</sub> introducing portion 10A. At this time, N<sub>2</sub> is also supplied into the exhaust pipe 42 at a flow rate of about 1 L/min to about 50 L/min as shown in FIG. 11 (Step 4C). After a predetermined period of time passes, the valve 23 is closed to stop the supply of TiCl<sub>4</sub> and at

the same time,  $TiCl_4$  remaining in the chamber 2 is exhausted from the chamber 2 (Step 5C).

[0099] After a predetermined period of time passes, the valve 33 is opened, so that  $NH_3$  is introduced from an  $NH_3$  introducing portion 5 10B (Step 6C). After a predetermined period of time passes, the valve 33 is closed to stop the supply of  $NH_3$ , and at the same time,  $NH_3$  and so on remaining in the chamber 2 are exhausted from the chamber 2 (Step 7C).

[0100] After a predetermined period of time passes, it is judged 10 whether or not 200 cycles of the treatment have been conducted (Step 8C). When it is judged that 200 cycles of the treatment have not been conducted, the processes from Step 4C to Step 7C are conducted again.

[0101] When it is judged that 200 cycles of the treatment have 15 been conducted, the valve 73 is closed to stop the supply of  $N_2$  to the exhaust pipe 42 (Step 9C). Thereafter, the wafer up/down pins 6 are moved up, so that the wafer W is detached from the susceptor 4 (Step 10C). Finally, the wafer W is carried out of the chamber 2 by the not-shown transfer arm (Step 11C).

20 [0102] In this embodiment, since the  $N_2$  supply system 70 to supply  $N_2$  is disposed in the exhaust pipe 42 that is on the downstream side of the dry pump 48, the clogging of the exhaust pipe 42 can be reduced. To be more specific, the inside of the exhaust pipe 42 that is on the downstream side of the dry pump 48 is kept at the atmospheric 25 pressure. Therefore, when  $N_2$  is supplied into the exhaust pipe 42 that is on the downstream side of the dry pump 48, the pressure of  $TiCl_4$  is lowered to reduce liquid  $TiCl_4$ . Further, the supply of  $N_2$  causes  $TiCl_4$  to be pushed out, so that  $TiCl_4$  is not easily adsorbed

by an inner wall of the exhaust pipe 42 and  $TiCl_4$  adsorbed by the inner wall of the exhaust pipe 42 is easily detached. Consequently, yellow powder adhering to the inner wall of the exhaust pipe 42 can be greatly reduced to reduce the clogging of the exhaust pipe 42.

5 As a result, maintenance frequency can be lowered.

(Fourth Embodiment)

[0103] Hereinafter, a fourth embodiment of the present invention will be explained. In this embodiment, the explanation will be given on an example where provided is a tape heater for heating an 10 exhaust pipe that is on a downstream side of a dry pump.

[0104] FIG. 12 is a schematic block diagram of a deposition device according to this embodiment. As shown in FIG. 12, a tape heater 80 for heating an exhaust pipe 42 is wound around an external wall of the exhaust pipe 42 that is on a downstream side of a dry pump

15 48. A tape heater controller 81 that controls the heating temperature of the tape heater 80 by adjusting an electric current passing through the tape heater 80 is electrically connected to the tape heater 80.

[0105] Hereinafter, the flow of the treatment conducted in a 20 deposition device 1 will be explained, following FIG. 13 and FIG. 14. FIG. 13 is a flowchart showing the flow of the treatment conducted in the deposition device 1 according to this embodiment, and FIG. 14 is a view schematically showing the treatment conducted in the deposition device 1 according to this embodiment.

25 [0106] The dry pump 48 is operated to conduct low evacuation of the inside of a chamber 2. Thereafter, the low evacuation by the dry pump 48 is changed to high evacuation by a turbo molecular pump 44 (Step 1D).

[0107] After the pressure inside the chamber 2 is reduced to, for example,  $1.33 \times 10^{-2}$  Pa or lower, a not-shown transfer arm holding a wafer W extends to carry the wafer W into the chamber 2 (Step 2D). Thereafter, wafer up/down pins 6 are moved down to place the wafer 5 W on a susceptor 4. Further, the exhaust pipe 42 is heated by the tape heater 80 to about 60°C to about 100°C (Step 3D).

[0108] After the temperature of the wafer W is raised and the temperature of the exhaust pipe 42 becomes stable at 60°C to 100°C, a valve 23 is opened while the pressure inside the chamber 2 is kept 10 at about 50 Pa to about 400 Pa, so that TiCl<sub>4</sub> is introduced from a TiCl<sub>4</sub> introducing portion 10A as shown in FIG. 14 (Step 4D). After a predetermined period of time passes, the valve 23 is closed to stop the supply of TiCl<sub>4</sub> and at the same time, TiCl<sub>4</sub> remaining in the chamber 2 is exhausted from the chamber 2 (Step 5D).

15 [0109] After a predetermined period of time passes, a valve 33 is opened, so that NH<sub>3</sub> is introduced from an NH<sub>3</sub> introducing portion 10B (Step 6D). After a predetermined period of time passes, the valve 33 is closed to stop the supply of NH<sub>3</sub>, and at the same time, NH<sub>3</sub> and so on remaining in the chamber 2 are exhausted from the chamber 20 2 (Step 7D).

[0110] After a predetermined period of time passes, it is judged whether or not 200 cycles of the treatment have been conducted (Step 25 8D). When it is judged that 200 cycles of the treatment have not been conducted, the processes from Step 4D to Step 7D are conducted again.

[0111] When it is judged that 200 cycles of the treatment have been conducted, the heating of the exhaust pipe 42 by the tape heater 80 is stopped (Step 9D). Thereafter, the wafer up/down pins 6 are

moved up, so that the wafer W is detached from the susceptor 4 (Step 10D). Finally, the wafer W is carried out of the chamber 2 by the not-shown transfer arm (Step 11D).

[0112] In this embodiment, since the tape heater 80 for heating 5 the exhaust pipe 42 that is on the downstream side of the dry pump 48 is provided, the clogging of the exhaust pipe 42 can be reduced. To be more specific, when the exhaust pipe 42 that is on the downstream side of the dry pump 48 is heated,  $TiCl_4$  is not easily liquefied and liquid  $TiCl_4$  is liable to turn into gas again. 10 Accordingly, liquid  $TiCl_4$  is reduced. Further, when the exhaust pipe 42 that is on the downstream side of the dry pump 48 is heated,  $TiCl_4$  adsorbed by an inner wall of the exhaust pipe 42 is easily detached from the inner wall of the exhaust pipe 42. Consequently, an amount of  $TiCl_4$  adhering to the inner wall of the exhaust pipe 15 42 is reduced. This makes it possible to greatly reduce yellow powder adhering to the inner wall of the exhaust pipe 42 to reduce the clogging of the exhaust pipe 42. As a result, maintenance frequency can be lowered.

(Fifth Embodiment)

20 [0113] Hereinafter, a fifth embodiment of the present invention will be explained. In this embodiment, the explanation will be given on an example where  $NH_3$  is supplied at a flow rate about 10 times as large as the flow rate of  $TiCl_4$  or at a larger flow rate.

[0114] FIG. 15 is a flow chart showing the flow of the treatment 25 conducted in a deposition device 1 according to this embodiment. Note that the deposition device of this embodiment is a similar one to the deposition device in the first embodiment, but the capturing unit 46 is not disposed.

[0115] A dry pump 48 is operated to conduct low evacuation of the inside of a chamber 2. Thereafter, the low evacuation by the dry pump 48 is changed to high evacuation by a turbo molecular pump 44 (Step 1E).

5 [0116] After the pressure inside the chamber 2 is reduced to, for example,  $1.33 \times 10^{-2}$  Pa or lower, a not-shown transfer arm holding a wafer W extends to carry the wafer W into the chamber 2 (Step 2E). Thereafter, wafer up/down pins 6 are moved down to place the wafer W on a susceptor 4 (Step 3E).

10 [0117] After the temperature of the wafer W is raised, a valve 23 is opened while the pressure inside the chamber 2 is kept at about 50 Pa to about 400 Pa, so that  $TiCl_4$  is introduced from a  $TiCl_4$  introducing portion 10A at a flow rate of about 30 sccm (Step 4E). After a predetermined period of time passes, the valve 23 is closed  
15 to stop the supply of  $TiCl_4$  and at the same time,  $TiCl_4$  remaining in the chamber 2 is exhausted from the chamber 2 (Step 5E).

[0118] After a predetermined period of time passes, a valve 33 is opened, so that  $NH_3$  is introduced from an  $NH_3$  introducing portion 10B at a flow rate of about 300 sccm to about 1000 sccm (Step 6E).

20 After a predetermined period of time passes, the valve 33 is closed to stop the supply of  $NH_3$ , and at the same time,  $NH_3$  and so on remaining in the chamber 2 are exhausted from the chamber 2 (Step 7E).

[0119] After a predetermined period of time passes, it is judged whether or not 200 cycles of the treatment have been conducted (Step 25 8E). When it is judged that 200 cycles of the treatment have not been conducted, the processes from Step 4E to Step 7E are conducted again.

[0120] When it is judged that 200 cycles of the treatment have

been conducted, the wafer up/down pins 6 are moved up, so that the wafer W is detached from the susceptor 4 (Step 9E). Finally, the wafer W is carried out of the chamber 2 by the not-shown transfer arm (Step 10E).

5 [0121] In this embodiment, since NH<sub>3</sub> is supplied at a flow rate about 10 times as large as the flow rate of TiCl<sub>4</sub> or at a larger rate, the clogging of an exhaust pipe 42 can be reduced. As a result, maintenance frequency can be lowered.

(Example)

10 [0122] Hereinafter, an example will be explained. In this example, the deposition device according to the fifth embodiment was used and the degree of the clogging of the exhaust pipe was observed.

15 [0123] Measurement conditions will be explained. In this example, a TiN film was formed on a wafer, using the deposition device according to the fifth embodiment. Incidentally, the TiN film with a thickness of about 10 nm was formed on each of the wafers. TiCl<sub>4</sub> was supplied at a flow rate of about 30 sccm and NH<sub>3</sub> was supplied at a flow rate of about 800 sccm. Further, for comparison with this 20 example, TiCl<sub>4</sub> was supplied at a flow rate of about 30 sccm and NH<sub>3</sub> was supplied at a flow rate of about 100 sccm, and the degree of the clogging of the exhaust pipe 42 in this case was also observed.

25 [0124] The measurement results will be discussed. When TiCl<sub>4</sub> was supplied at a flow rate of about 30 sccm and NH<sub>3</sub> was supplied at a flow rate of about 100 sccm, the exhaust pipe was clogged at the time after the TiN film was formed on 30 pieces of the wafer and maintenance was required. On the other hand, when TiCl<sub>4</sub> was supplied at a flow rate of about 30 sccm and NH<sub>3</sub> was supplied at a flow rate

of about 800 sccm, even the TiN film formation on 100 pieces of the wafers did not cause the exhaust pipe to be clogged, and maintenance was not required. It has been confirmed from these results that the supply of NH<sub>3</sub> at a flow rate about 10 times as large as the flow 5 rate of TiCl<sub>4</sub> or at a larger rate reduces the clogging of the exhaust pipe to lower maintenance frequency.

(Sixth Embodiment)

[0125] Hereinafter, a sixth embodiment of the present invention will be explained. In this embodiment, the explanation will be 10 given on an example where NH<sub>3</sub> is periodically supplied into an exhaust pipe while a deposition device does not have a wafer carried therein.

[0126] FIG. 16 is a flowchart showing the flow of the overall treatment conducted in the deposition device according to this embodiment, FIG. 17 is a flowchart showing the flow of the treatment 15 for one piece of wafer conducted in the deposition device according to this embodiment, and FIG. 18 is a view schematically showing the treatment conducted in the deposition device according to this embodiment. The deposition device of this embodiment is a similar one to the deposition device of the first embodiment, but the 20 capturing unit 46 is not disposed.

[0127] First, a TiN film is formed on the first wafer W (Step 1F). Concretely, high evacuation is first conducted by a turbo molecular pump 44 (Step 101F). After the pressure inside a chamber 2 is reduced to, for example,  $1.33 \times 10^{-2}$  Pa or lower, the first wafer W is carried 25 into the chamber 2 and placed on a susceptor 4 thereafter (Step 102F, Step 103F). After the temperature of the wafer W is raised, TiCl<sub>4</sub> is introduced from a TiCl<sub>4</sub> introducing portion 10A at a flow rate of about 30 sccm (Step 104F). Thereafter, the supply of TiCl<sub>4</sub> is

stopped, and at the same time,  $TiCl_4$ , remaining in the chamber 2 is exhausted from the chamber 2 (Step 105F). After a predetermined period of time passes,  $NH_3$ , is introduced at a flow rate of about 100 sccm (Step 106F). Thereafter, the supply of  $NH_3$ , is stopped, and

5 at the same time,  $NH_3$ , and so on remaining in the chamber 2 are exhausted from the chamber 2 (Step 107F). After a predetermined period of time passes, it is judged whether or not 200 cycles of the treatment have been conducted (Step 108F). When it is judged that 200 cycles of the treatment have not been conducted, the

10 processes from Step 104F to Step 107F are conducted again. When it is judged that 200 cycles of the treatment have been conducted, the wafer W is detached from the susceptor 4, and the first wafer W is carried out of the chamber 2 by a not-shown transfer arm (Step 109F, Step 110F).

15 [0128] Subsequently, the same processes as in Step 101F to Step 110F are also conducted for the second, third, ..., twenty-fifth wafers W respectively (Step 2F to Step 25F).

[0129] After the twenty-fifth wafer W is carried out of the chamber 2, a valve 33 is opened while the turbo molecular pump 44 and a dry pump 48 are in operation, so that  $NH_3$ , is introduced from an  $NH_3$ , introducing portion 10B at a flow rate of about 300 sccm to about 1000 sccm, as shown in FIG. 18 (Step 26F). The introduced  $NH_3$ , is supplied into an exhaust pipe 42 that is on a downstream side of the dry pump 48 via the chamber 2. The supply of  $NH_3$ , while the

20 deposition device 1 does not have the wafer W carried therein is conducted periodically. Specifically, it is conducted for, for example, every 1 lot (25 pieces of the wafers). After a

25 predetermined period of time passes, the valve 33 is closed to stop

the supply of  $\text{NH}_3$  (Step 27F).

[0130] In this embodiment, since  $\text{NH}_3$  is supplied into the exhaust pipe 42 while the deposition device 1 does not have the wafer W carried therein, the clogging of the exhaust pipe 42 can be reduced.

5 Therefore, the frequency for removing yellow powder by opening the exhaust pipe 42 can be lowered.

[0131] It should be noted that the present invention is not limited to the described contents in the above embodiments, and the structure, the materials, the arrangement of each member, and so 10 on are appropriately changeable within a range not departing from the spirit of the present invention. Table 1 presents examples of treatment gases for forming film species and these films.  $\text{TiCl}_4$  and  $\text{NH}_3$  are used in the first embodiment and the third to sixth 15 embodiments, and  $\text{TiCl}_4$ ,  $\text{SiH}_2\text{Cl}_2$ , and  $\text{NH}_3$  are used in the second embodiment, but the treatment gases shown in Table 1 are also usable.

[Table 1]

Film Species	First Treatment Gas	Second Treatment Gas	Third Treatment Gas	Film Species	First Treatment Gas	Second Treatment Gas	Third Treatment Gas
TiN	$\text{TiCl}_4$	$\text{NH}_3$	-	TaN	$\text{TaF}_5$	$\text{NH}_3$	-
	$\text{TiF}_4$	$\text{NH}_3$	-		$\text{TaCl}_5$	$\text{NH}_3$	-
	$\text{TiBr}_4$	$\text{NH}_3$	-		$\text{TaBr}_5$	$\text{NH}_3$	-
	$\text{TiI}_4$	$\text{NH}_3$	-		$\text{TaI}_5$	$\text{NH}_3$	-
	TEMAT	$\text{NH}_3$	-		TBTDET	$\text{NH}_3$	-
	TDMAT	$\text{NH}_3$	-	TaSiN	$\text{TaF}_5$	$\text{NH}_3$	$\text{SiH}_4$
	TDEAT	$\text{NH}_3$	-		$\text{TaCl}_5$	$\text{NH}_3$	$\text{SiH}_4$
TiSiN	$\text{TiCl}_4$	$\text{NH}_3$	$\text{SiH}_4$		$\text{TaBr}_5$	$\text{NH}_3$	$\text{SiH}_4$
	$\text{TiF}_4$	$\text{NH}_3$	$\text{SiH}_4$		$\text{TaI}_5$	$\text{NH}_3$	$\text{SiH}_4$
	$\text{TiBr}_4$	$\text{NH}_3$	$\text{SiH}_4$		TBTDET	$\text{NH}_3$	$\text{SiH}_4$
	$\text{TiI}_4$	$\text{NH}_3$	$\text{SiH}_4$		$\text{TaF}_5$	$\text{NH}_3$	$\text{Si}_2\text{H}_6$
	TEMAT	$\text{NH}_3$	$\text{SiH}_4$		$\text{TaCl}_5$	$\text{NH}_3$	$\text{Si}_2\text{H}_6$
	TDMAT	$\text{NH}_3$	$\text{SiH}_4$		$\text{TaBr}_5$	$\text{NH}_3$	$\text{Si}_2\text{H}_6$
	TDEAT	$\text{NH}_3$	$\text{SiH}_4$		$\text{TaI}_5$	$\text{NH}_3$	$\text{Si}_2\text{H}_6$
	$\text{TiCl}_4$	$\text{NH}_3$	$\text{Si}_2\text{H}_6$		TBTDET	$\text{NH}_3$	$\text{Si}_2\text{H}_6$
	$\text{TiF}_4$	$\text{NH}_3$	$\text{Si}_2\text{H}_6$		$\text{TaF}_5$	$\text{NH}_3$	$\text{SiH}_2\text{Cl}_2$

$TiBr_4$	$NH_3$	$Si_2H_6$	$TaCl_5$	$NH_3$	$SiH_2Cl_2$
$TiI_4$	$NH_3$	$Si_2H_6$	$TaBr_5$	$NH_3$	$SiH_2Cl_2$
TEMAT	$NH_3$	$Si_2H_6$	$TaI_5$	$NH_3$	$SiH_2Cl_2$
TDMAT	$NH_3$	$Si_2H_6$	TBTDET	$NH_3$	$SiH_2Cl_2$
TDEAT	$NH_3$	$Si_2H_6$	$TaF_5$	$NH_3$	$SiCl_4$
$TiCl_4$	$NH_3$	$SiH_2Cl_2$	$TaCl_5$	$NH_3$	$SiCl_4$
$TiF_4$	$NH_3$	$SiH_2Cl_2$	$TaBr_5$	$NH_3$	$SiCl_4$
$TiBr_4$	$NH_3$	$SiH_2Cl_2$	$TaI_5$	$NH_3$	$SiCl_4$
$TiI_4$	$NH_3$	$SiH_2Cl_2$	TBTDET	$NH_3$	$SiCl_4$
TEMAT	$NH_3$	$SiH_2Cl_2$	$Al_2O_3$	$Al(CH_3)_3$	$H_2O$
TDMAT	$NH_3$	$SiH_2Cl_2$		$Al(CH_3)_3$	$H_2O_2$
TDEAT	$NH_3$	$SiH_2Cl_2$	$ZrO_2$	$Zr(O-t(C_4H_9))_4$	$H_2O$
$TiCl_4$	$NH_3$	$SiCl_4$		$Zr(O-t(C_4H_9))_4$	$H_2O_2$
$TiF_4$	$NH_3$	$SiCl_4$		$ZrCl_4$	$H_2O$
$TiBr_4$	$NH_3$	$SiCl_4$		$ZrCl_4$	$H_2O_2$
$TiI_4$	$NH_3$	$SiCl_4$	$Ta_2O_5$	$Ta(OC_2H_5)_5$	$O_2$
TEMAT	$NH_3$	$SiCl_4$		$Ta(OC_2H_5)_5$	$H_2O$
TDMAT	$NH_3$	$SiCl_4$		$Ta(OC_2H_5)_5$	$H_2O_2$
TDEAT	$NH_3$	$SiCl_4$			

[0132]  $TiCl_4$  and  $NH_3$  are supplied in the order of  $TiCl_4$  and  $NH_3$  in the first embodiment and the third to sixth embodiments described above, and  $TiCl_4$ ,  $SiH_2Cl_2$ , and  $NH_3$  are supplied in the order of  $TiCl_4$ ,  $SiH_2Cl_2$ , and  $NH_3$  in the second embodiment, but the supply order is not limited to these orders. The same applies to the treatment gases shown in the aforesaid Table 1.

[0133] The capturing unit 46 is disposed in the third embodiment, but the structure in which the capturing unit 46 is not disposed may also be adopted. The tape heater 80 may be wound around as in the fourth embodiment. Further,  $N_2$  is supplied into the exhaust pipe 42, but other inert gas may be supplied. Moreover, though  $N_2$  is supplied into the exhaust pipe 42 at the time of the supply of  $TiCl_4$ , it is also possible to start supplying  $N_2$  into the exhaust pipe 42 before the supply of  $TiCl_4$ .

[0134] In the fourth embodiment, the exhaust pipe 42 is heated to  $60^\circ C$  to  $100^\circ C$ , but the heating temperature is not limited to a specific value as long as it is the temperature causing the

evaporation of the metal-containing gas. For example, when the metal-containing gas is  $TaF_5$  or  $TaCl_5$ , the exhaust pipe 42 is heated to 80°C to 200°C. When the metal-containing gas is  $Al(CH_3)_3$ ,  $Zr(O-t(C_4H_9))_4$ , or  $Ta(OC_2H_5)_5$ , the exhaust pipe 42 is heated to 80°C to 150°C. Further, the exhaust pipe 42 is heated after the wafer W is carried in, but it is also possible to start heating the exhaust pipe 42 before the wafer W is carried in or while the wafer W is being carried in.

5 [0135] In the fourth embodiment, the capturing unit 46 is disposed, but the structure without the capturing unit 46 may also be adopted. The tape heater 80 is wound around the exhaust pipe 42, but any other type is usable as long as it can heat the exhaust pipe 42.

10 [0136] In the fifth and sixth embodiments, any of the capturing unit 46, the  $N_2$  supply system 70, and the tape heater 80 is not disposed, but it is also possible to dispose at least one of these components. In these cases, a larger amount of  $TiCl_4$  can be captured.

15 [0137] In the first to sixth embodiments, the wafer W is used, but a glass substrate may be used. Further, the explanation is given on the deposition device 1 that forms a film by alternately supplying  $TiCl_4$  and  $NH_3$  or by supplying  $TiCl_4$ ,  $SiH_2Cl_2$ , and  $NH_3$  by turns, but the present invention is also applicable to a deposition device that forms a film by supplying these gases simultaneously.

20 [0138] In the first to sixth embodiments, the chamber 2 is evacuated to exhaust  $TiCl_4$  and so on, but it is also possible to supply a purge gas such as  $N_2$  into the chamber 2 at the time of the evacuation. It is also possible to repeat the supply of the purge gas and vacuuming. Moreover, the present invention is applicable

to an etching apparatus, not limited to the deposition device. In this case, at least two kinds of etching gases may be alternately supplied or simultaneously supplied.